

FLUID CRACKING CATALYST WITH CARBON SELECTIVITY

M. L. Occelli* and D. C. Kowalczyk
Gulf Research & Development Company
P. O. Drawer 2038
Pittsburgh, PA 15230

ABSTRACT

A fluid cracking catalyst was formed by spray drying a silica sol slurry containing an acid-leached kaolin mineral (with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.6) and calcined rare earth exchanged zeolite Y (CREY). Microactivity testing (MAT) data show the catalyst (with ~22% CREY) can give 66 vol% conversion in the presence of 5000 ppm Ni-Equivalents. Carbon generation (4.3%) seems to be independent of metals concentration over the range investigated. In the presence of 1.0% vanadium, the catalyst is as active as when metal-loaded with 5000 ppm Ni-Equivalents. With 2% vanadium, there is a drastic decrease in activity. Commercial catalysts have similar activity and gasoline selectivity but generate considerably more hydrogen and carbon, especially at high metals loading.

INTRODUCTION

Oil shortages have, at the present, disappeared, but refiners are nonetheless under economic pressure to process cheaper, metals-contaminated crudes. In fact, because of nationwide conservation efforts, gasoline consumption in the U.S. has and is projected to steadily decline in the 80's. Therefore, refiners without the capability of converting less costly, heavier oils into transportation liquids will suffer competitively in this shrinking energy market (4-6). Several units have already reported using heavy crudes in their FCC operations (7-9).

Catalyst requirements to process Ni- and V-contaminated feedstocks have been described elsewhere; (9-11) a recent discussion has been given by Magee (6). Vanadium is known to destroy catalyst activity, and its effects can be mitigated by tin addition (12). Nickel, while not causing zeolite destruction, generates large amounts of gases and coke, placing severe demands on gas compressors' capability. Antimony organics have been shown to reduce by 50% gas formation due to metal contaminants, especially nickel (13-15). Cracking catalysts capable of forming inactive metal silicates or even aluminosilicates on their surface could crack heavy oils to useful products and minimize coke, hydrogen, and light gas generation.

Examples of silica-bound zeolite containing FCC have been described by Elliot (16), Ostermaier and Elliot (17), Flaherty et al. (18), and Seese et al. (19). It is the purpose of this paper to report a silica-rich cracking catalyst resistant to deactivation by metals contaminants like nickel and vanadium.

*To whom all correspondence should be addressed.

EXPERIMENTAL

Catalyst Preparation

A silica sol was prepared by simultaneously mixing diluted sodium silicate, alum, and sulphuric acid in a manner to keep the slurry pH between 2.8 and 3.2. The sol was then vigorously homogenized and aged for three hours at room temperature. Calcined and acid-washed kaolin ($\text{SiO}_2/\text{Al}_2\text{O}_3=2.6$) was then added to form a slurry containing 639 g SiO_2 , 231.6 g Al_2O_3 , and 126 g clay. Calcined rare earth exchanged zeolite Y (CREY from Davison) was then added to obtain the desired cracking activity. The catalyst zeolite level (% CREY) is defined as $\text{CREY}/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CLAY} + \text{CREY}) \cdot 100$.

The fluidized cracking catalyst was obtained by spray drying the slurry at ~15-20% solids. The microspheres were slurried in a 5 l 2% NH_4OH solution to remove sodium ions. After a final washing with a large excess of deionized water and drying at 400°C for 10 h, the catalysts were submitted for evaluation. The microspheres with ~22% CREY had 250 m^2/g BET surface area, 0.23 cc/g pore volume, and an average pore radius of 18.6 Å; their bulk density was 0.66 g/cc.

Catalyst Testing

Catalytic evaluation was performed using a microactivity test similar to the one described by Ciappetta and Henderson (1). The weight hourly space velocity was 15 with 80 sec catalyst contact time at $T = 480^\circ\text{C}$. The charge stock was a Kuwait gas oil having a 260°-426°C boiling range (see Table 1); a catalyst-to-oil ratio of 2.5 was used. Prior to testing, catalysts were steam-aged for 10 h at 730°C with a ~50-50% N_2 -steam mixture. (Ni-V) naphthenates were used to metal-load fresh catalysts according to a procedure described elsewhere (2). Ni-equivalents is defined as the sum $(\text{Ni} + 1/5 \text{ V})$ expressed in parts per million (ppm). Percent conversion is defined as: $(V_f - V_p) 100/V_f$ where V_f is the volume of the fresh feed (FF) and V_p is the volume of product boiling above 204°C.

RESULTS AND DISCUSSION

As expected (3), cracking activity of this silica-rich catalyst increases with zeolite content (Figure 1). In the 15-22% CREY range, conversion changed from 74 to 81.6%. Gasoline make remained at ~53%; this and the increase in hydrogen and carbon generation indicates the occurrence of overcracking, Figures 2, 3, and 4.

Metals $(\text{Ni} + 1/5 \text{ V})$ effects on catalyst activity are given in Figures 5-8. Losses in gasoline yields follow the decrease in catalyst activity with metal loadings (Figures 5 and 6) since both effects are due to losses in catalyst crystallinity. The silica-rich catalyst (with 15 or 22% CREY) deactivates in a manner similar to that of a commercial catalyst having comparable initial activity (Figure 5). The catalyst (with ~22% CREY) appears to be more selective with respect to hydrogen generation (Figure 7), and its carbon make (~4.3%) is independent of metals loading up to 5000 Ni-Equivalents. In contrast, the commercial catalyst carbon generation monotonically increases with metals level (Figure 8). Both catalysts have similar resistance to vanadium poisoning. In the presence of 1.0% V conversion was ~60% (down from ~82% for the fresh catalysts); with 2% V, cracking activity was reduced to ~30%. The silica-rich matrix of the catalyst did not prevent zeolite destruction by the vanadium. CREY has a strong diffraction peak at $2\theta=23.8^\circ$. With 1% V, the original peak intensity was reduced by ~50%; with 2% V, evidence of crystallinity disappeared.

Results in Table 2 show the silica-rich catalyst's hydrothermal stability (50/50% nitrogen-steam for 10 h at 730°C) and carbon selectivity. Even after steaming at 815°C for 5 h with 95% steam the catalyst was able to retain 90% of the cracking activity measured after aging with 50% steam. Steaming, however, affects the stability of vanadium-contaminated catalysts. In fact, after aging with 95% steam (10 h at 730°C) microspheres with 0.5% V retained ~70% of their initial activity; with 0.75% V, they became inactive. X-ray diffractograms showing crystallinity losses due to vanadium loadings are given in Figure 9.

Without metals, the steam-aged catalyst had 177.8 m²/g BET surface area, 0.19 cc/g nitrogen pore volume, and an average pore radius of 21.2 Å. In Figure 10 its carbon selectivity is represented as the weight of carbon by-product per volume percentage of conversion. This value is plotted as a function of conversion to show that for conversion levels in the 65 to 80% range, the silica-rich catalyst generates lower coke yields than the commercial cracking catalysts tested.

The use of acid-leached calcined kaolin has little effect on a fresh catalyst (with ~15% CREY) activity, but it may increase gasoline yields, see Table 3. The catalyst exhibits improved resistance to metals deactivation when it contains an acid-leached calcined kaolin mineral (with SiO₂/Al₂O₃ = 2.6) instead of untreated kaolin. The acid treatment removes aluminum and establishes octahedral vacancies in the mineral lattice. These "holes" could host metals like Ni and V and negate their deleterious effects on cracking activity and product selectivities. The catalyst's low carbon generation has probably been enhanced by its silica-rich matrix's ability to form inert nickel silicates. Nickel passivation, due to silicates formation, has been previously postulated by Meisenheimer (20) for amorphous (silica-alumina) cracking catalysts.

REFERENCES

1. F. Ciapetta and D. Henderson, *Oil and Gas Journal*, 65, 88 (1967).
2. B. R. Mitchell, *Ind. Eng. Chem. Prod. Res. Dev.*, 19, 209 (1980).
3. J. S. Magee and J. J. Blazek, "Zeolite Chemistry and Catalysis," ACS Monograph #171, J. A. Rabo, Ed., 615 (1976).
4. C. P. Reeg, *NPRA Annual Meeting*, AS82-3, 1 (1982).
5. C. P. Carter, *Hydro. Proc.*, 96 (1981).
6. J. S. Magee, "Adv. in Cat. Chem., II Symposium," Salt Lake City, Utah (1982).
7. J. R. Murphy and A. K. Logwinuk, *NPRA Annual Meeting*, AMS1-29, 11 (1981).
8. R. E. Ritter et al., *NPRA Annual Meeting*, AM81-44, 1-4 (1981).
9. R. E. Ritter et al., *Oil and Gas Journal*, 103 (1981).
10. R. N. Cimbalo et al., *Oil and Gas Journal*, 112 (1972).
11. J. G. Sikonia et al., *Oil and Gas Journal*, 141 (1981).
12. A. English and D. C. Kowalczyk, *Oil and Gas Journal* (1984), to be submitted.
13. J. R. Murphy in "Sym. Prod., Character., Process of Heavy Oils, etc.," University of Utah, 5 (1981).

14. J. W. Gall et al., NPRA Annual Meeting, AM82-50, 5 (1982).
15. D. L. McKay and B. J. Bertus, "Symp. on Advances in Petr. Proc.," Div. of Petr. Chemistry Preprints 24, 2, 645 (1979).
16. C. H. Elliot, Jr., U.S. Patent No. 3,867,308 (1975).
17. J. J. Ostermaier and C. H. Elliot, Jr., U.S. Patent No. 3,957,689 (1976).
18. T. V. Flaherty, Jr., et al., U.S. Patent No. 4,126,579 (1978).
19. M. A. Seese et al., U.S. Patent No. 4,226,743 (1980).
20. R. G. Meisenheimer, J. Cat., 1, 356 (1962).

WPC#4082

Table 1. Kuwait gas oil inspections.

Gravity, API	23.5
Viscosity, 130°F	94.7
Viscosity, 150°F	70.5
Viscosity, 210°F	50.8
Pour Point, °F	+80
Nitrogen, wt%	0.074
Sulfur, wt%	2.76
Carbon, Res., wt%	0.23
Bromine No.	5.71
Aniline Point, °F	176.5
Nickel, ppm	<0.1
Vanadium, ppm	<0.1
Distillation, at 760 mm	
End Point, °C	426
5 Pct. Cond.	263
Approx. Hydrocarbon	
Type Analysis: vol%	
Carbon as Aromatics	23.1
Carbon as Naphthenes	10.5
Carbon as Paraffins	66.3

Table 2. Hydrothermal stability data of a SiO_2 -rich cracking catalyst containing ~22% CREY. Steaming was performed with a 50-50% steam-nitrogen mixtures at 1 atm for 10 h.

	<u>Steaming Temperature ($^{\circ}\text{C}$)</u>		
	<u>730</u>	<u>760</u>	<u>790</u>
Conversion (V%ff)	81.26	80.06	76.03
Gasoline (V%ff)	52.83	54.92	52.45
Hydrogen (wt%ff)	0.03	0.02	0.02
Carbon (wt%ff)	3.99	3.56	3.20

Table 3. Effects of an acid-leached kaolin mineral on the metals resistance of a FCC containing ~15% CREY. Test conditions: $T = 480^{\circ}\text{C}$, Kuwait G0; aging with 50% steam for 10 h at 730°C .

Kaolin ($\text{SiO}_2/\text{Al}_2\text{O}_3$)	2.6	2.6	2.0	2.0
Metals (Ni-Equiv.)	0	3000	0.0	3000
Conversion (V%ff)	72.2	62.9	72.9	51.0
Gasoline (V%ff)	52.1	42.5	50.2	32.9
Hydrogen (wt%ff)	0.05	0.50	0.03	0.44
Carbon (wt%ff)	2.78	2.94	2.46	3.04

Figure 1 Cracking Activity

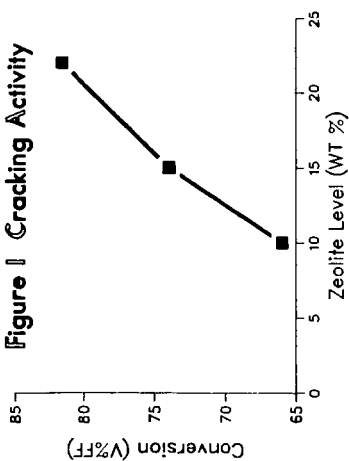


Figure 3 Hydrogen Yields

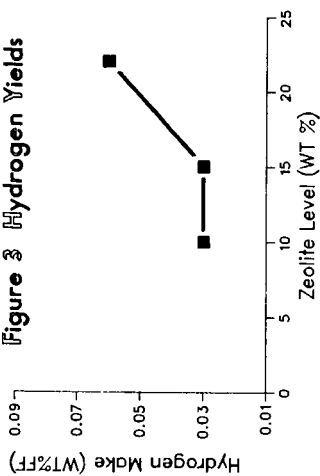


Figure 2 Gasoline Yields

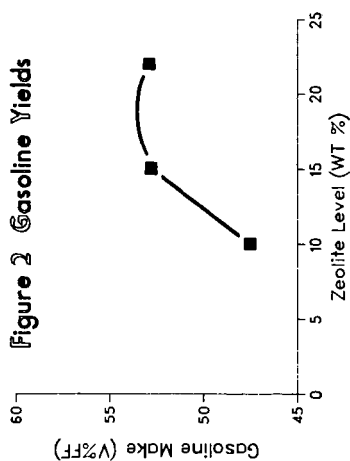


Figure 4 Carbon Yields

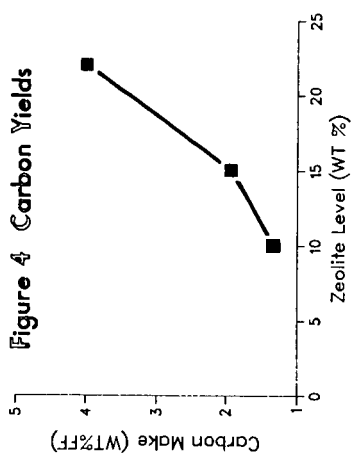


Figure 5 Metal (Ni + V) Effects on Catalyst Activity

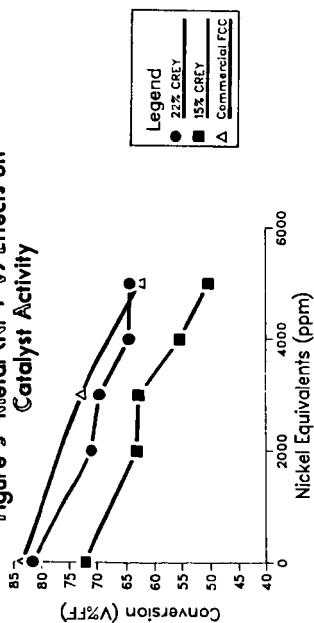


Figure 7 Metal (Ni + V) Effects on Hydrogen Make

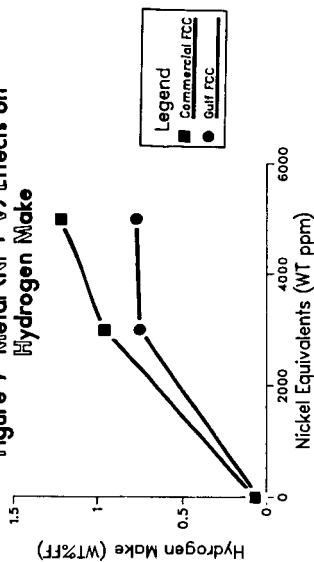


Figure 6 Metal (Ni + V) Effects on Gasoline Generation

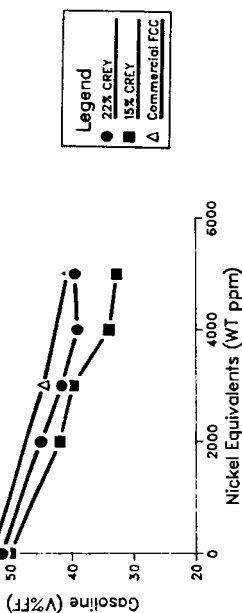


Figure 8 Metal (Ni + V) Effects on Carbon Make

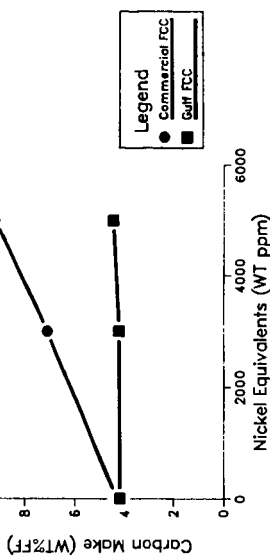


FIGURE 9:

X-RAY DIFFRACTOGRAMS SHOWING VANADIUM EFFECTS ON CRYSTALLINITY. CATALYSTS WERE STEAMED FOR 10h AT 730°C, WITH 95% STEAM AT 1atm.

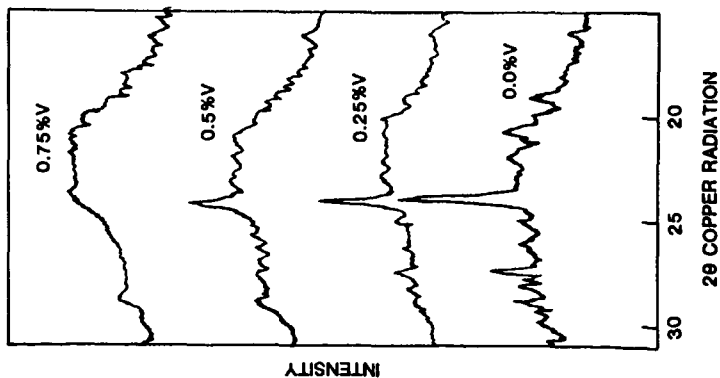


FIGURE 10
GULF SILICA-RICH FCC CATALYST
MAT CARBON SELECTIVITY

